

L Number	Hits	Search Text	DB	Time stamp
2	7	(selectively with depositing same silicide) and (in adj situ)	USPAT; US-PGPUB	2003/03/06 12:58
3	2	(selectively with depositing same silicide) and ((in adj situ) with deposit\$3)	USPAT; US-PGPUB	2003/03/06 12:59
4	575	((in adj situ) with deposit\$3)	USPAT; US-PGPUB	2003/03/06 13:04
5	453	((in adj situ) with deposit\$3)) and substrate	USPAT; US-PGPUB	2003/03/06 13:04
6	9	((in adj situ) with deposit\$3)) and substrate) and (selectively with depositing)	USPAT; US-PGPUB	2003/03/06 13:01
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8	21	((in adj situ) with deposit\$3)) and substrate	EPO; JPO; DERWENT; IBM TDB	2003/03/06 13:07
14	3074	438/642-644,648-652,655,674-675,682.ccls.	USPAT; US-PGPUB	2003/03/06 13:33
15	44	438/642-644,648-652,655,674-675,682.ccls. and silicide and (in adj situ)	USPAT; US-PGPUB	2003/03/06 13:40
17	2	("6204175") or ("5856236")).PN.	USPAT; US-PGPUB	2003/03/06 13:41

US-PAT-NO: 5989999

DOCUMENT-IDENTIFIER: US 5989999 A

TITLE: Construction of a tantalum nitride film on a semiconductor wafer

----- KWIC -----

In manufacturing an integrated circuit, it is desirable to perform successive steps of the manufacturing process, such as deposition and post-deposition processing, in the same chamber ("in-situ"). In-situ operations reduce the amount of contamination that a wafer is exposed to by decreasing the number of times that the wafer is required to be transferred between different pieces of manufacturing equipment. In-situ operations also lead to a reduction in the number of expensive pieces of manufacturing equipment that an integrated circuit manufacturer must purchase and maintain.

## 2. A Chamber for In-situ Operations

The present invention is not limited to titanium nitride barrier layers. The present invention may also improve properties and chemical compositions of other materials such as aluminum, copper, tantalum, tantalum pentoxide, silicides, other nitrides. For example, properties and chemical compositions of binary metal nitride  $M_{\text{sub}.x}N_{\text{sub}.y}$  and ternary metal silicon nitride  $M_{\text{sub}.x}Si_{\text{sub}.y}N_{\text{sub}.z}$  (where M may be Ti, Zr, Hf, Ta, Mo, W and other metals) may be improved by practicing aspects of the present invention. Substrates other than a silicon wafer can also be used such as stainless steel,

metals, oxides, glasses, and silicides.

US-PAT-NO: 4668530

DOCUMENT-IDENTIFIER: US 4668530 A

TITLE: Low pressure chemical vapor deposition of refractory metal silicides

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This invention relates to a process and apparatus for the Low Pressure Chemical Vapor Deposition (LPCVD) of polycrystalline refractory metal silicides, such as  $\text{TiSi}_{2.2}$ , in a reactor. An oxidized Si wafer is loaded in the reactor. The reactor is pumped down to a pressure of about  $10^{-7}$  Torr, or less. The Si substrate is heated to the predetermined deposition temperature of about  $630^{\circ}\text{C}$ . while avoiding heating of the reactor walls. The reactor is then purged with an inert gas, such as nitrogen. Next, polysilicon is deposited on the wafer by introducing  $\text{SiH}_4$  into the reactor at a pressure in the order of 0.2 Torr. A layer of polycrystalline titanium silicide is then formed on the polysilicon layer by introducing reactants, such as  $\text{TiCl}_4$  and  $\text{SiH}_4$ , into the reactor at deposition temperatures between about  $650^{\circ}\text{C}$ . to  $700^{\circ}\text{C}$ . and pressures of between about 50 to 460 m Torr.

This invention is in the field of semiconductors and more specifically formation of polycrystalline titanium silicide films on substrates.

Refractory metal silicides are most commonly prepared by some form of Physical Vapor Deposition (PVD) process, such as, sputtering or

co-evaporation.

However, Chemical Vapor Deposition (CVD) with its advantages of good conformal coverage, high throughput and purity promises to be a much better method of depositing refractory metal silicide films.

A particularly excellent candidate metal silicide material is  $\text{TiSi}_2$  because of its lower resistivity compared to other refractory metal silicides.

First, the substrate, preferably a cleaned and oxidized Si wafer, is loaded in a reactor. Next, the lines connecting the pump to the reactor chamber are opened to the pump so that pressure in the system is lowered. The Si substrate is heated to the predetermined deposition temperature of about 630.degree. C. while keeping the reactor walls cold. Keeping the walls cold prevents depositions on the walls and out-diffusion of impurities from the walls. Concurrently, the reactor is cyclically purged with an inert gas, such as nitrogen to bring the pressure down to  $10^{-7}$  Torr as measured by a capacitance gauge coupled to the reactor chamber. Next, polysilicon is deposited on the wafer by introducing a silicon reactant,  $\text{SiH}_4$ , into the reactor while maintaining a pressure on the order of  $2 \times 10^{-1}$  Torr. A layer of polycrystalline titanium silicide is then formed on the polysilicon layer by introducing silicon atom and titanium atom containing gaseous reactants, such as  $\text{TiCl}_4$  and  $\text{SiH}_4$ , into the reactor at substrate deposition temperatures between about 650.degree. to 700.degree. C. and chamber pressures of between about 50 to  $460 \times 10^{-3}$  Torr.

The reactor system is a Low Pressure CVD (LPCVD) reactor system for producing

metal silicides, such as titanium disilicide ( $\text{TiSi}_{2.2}$ ) films from reactants containing Si atoms, i.e., silane ( $\text{SiH}_{4.4}$ ) as a silicon source and metal atoms, i.e., titanium tetrachloride ( $\text{TiCl}_{4.4}$ ) as a metal source. As previously stated,  $\text{TiSi}_{2.2}$  is a preferred film material because of its lower resistivity compared to other refractory metal silicides. However, the invention is not intended to be limited to production of  $\text{TiSi}_{2.2}$  films., but other refractory metal silicide films, such as  $\text{MoSi}_{2.2}$ ,  $\text{WSi}_{2.2}$  and  $\text{TaSi}_{2.2}$  are contemplated as well.

Next, the chamber pressure (50-460 m Torr) and the wafer temperature (650.degree.-700.degree. C.) are established for the titanium silicide deposition. The cold trap 40 is immersed in a -60.degree. C. bath 41. Then the needle valve 62 is set to let a desired flow of  $\text{TiCl}_{4.4}$  into the chamber.

Sequential films of polysilicon and titanium silicide have been deposited, as above, at temperatures ranging from 650.degree. to 700.degree. C. and at pressures of 50 to 460 m Torr and at various ratios of  $\text{TiCl}_{4.4}$  /  $\text{SiH}_{4.4}$  flow rates. Some representative results under typical deposition conditions are summarized in Table I below:

Rutherford Backscattering Spectroscopy was used to determine the Si/Ti ratio and the thickness of these films. Sheet resistances were measured by the four point probe technique. Auger analysis was performed to determine the impurity concentration. A surface profilometer was used to confirm the thicknesses of the titanium silicide and polysilicon films and it also gave a measure of the surface roughness of the silicide films.

X-ray diffraction studies of these films show (See FIG. 2) that the as-deposited titanium silicide films are polycrystalline. It is also important to note that in the as-deposited condition, the most stable phase, i.e.,  $\text{TiSi}_{1.5}$ , is predominant. Thus, no additional processing step, such as annealing, is required after deposition to obtain this stable phase.

The underlying polysilicon peaks can also be identified in this spectrum. Within limits of Auger detection, no impurities, such as oxygen and carbon, were observed except for one film (film #2, table I). A leak in the vacuum system is believed to have caused this oxygen incorporation. It should be noted that the resistivity of this film is very high (150 micro-ohms-cm) due to the presence of oxygen in the silicide film, which points to the importance of having an oxygen free environment during silicide formation.

Sheet resistances of less than 1.1 ohms/square with film thicknesses from 2000 to 15500 Å have been obtained. These correspond to a minimum resistivity of 22 micro ohms-cm to a highest value of approximately 39 micro ohms-cm (excluding film #2, Table I) of the as-deposited silicide films. Even though an ideal Si/Ti ratio of close to 2 was obtained in most of these films, the resistivity variation from film to film is due to the difficulty in measuring the thickness of some of the films accurately. The surface smoothness of the silicide films varied from approximately 50 Å to about 1000 Å in the thickest film (film #4, Table I). The as-deposited films were annealed at 850°C for 15 minutes in an argon ambient. No changes were observed

in the already present titanium silicide phases indicating that the as-deposited films were already in this final stable form.

In summary, the LPCVD reactor of the invention is capable of in-situ sequential deposition of polysilicon and titanium silicide. As-deposited polycrystalline films of titanium silicide with good surface smoothness, low resistivity and uniformity have been obtained in this manner.

Tungsten silicide (WSi.sub.2) films can be formed in accordance with the above described process and apparatus by employing tungsten hexafluoride (WF.sub.6) as a gaseous reactant source of tungsten in place of titanium tetrachloride (TiCl.sub.4). The deposition temperature in this case would be about 450.degree. C. After deposition, annealing of the film in-situ at elevated temperatures for a short period may be desirable to assure that the film will be in the most stable di-silicide phase, i.e., WSi.sub.2.

Similarly, tantalum silicide films may be deposited by substituting tantalum pentachloride (TaCl.sub.5) as the metal containing reactant and depositing the TaSi.sub.2 film at about 625.degree. C. followed by annealing at elevated temperature, as required, to obtain the stable phase. In like manner, molybdenum (Mo) silicide films may be formed.

TABLE I \_\_\_\_\_ Deposition Conditions and Properties of As-Deposited LPCVD Titanium Silicide Films  
Film 1 Film 2.sup.a  
Film 3 Film 4 Film 5

						Pressure (Torr)			
0.5	0.063	0.15	0.65	0.46	Silane Flow	20.4	20.4	21.4	21.4
Rate (sccm)									
Needle Valve						4	4	4	1/2
(.OMEGA./quadrature.)						1	4	1.1	
0.25	0.38	Thickness (.ANG.)		2600	3800	2000	15500	8400	



Resistivity 26 152 22  
39 32 (u.OMEGA.-cm) Atomic Ratio 2.0 1.8 2.1 1.9 2.3  
(Si/Ti)

.sup.a Auger

detected a high oxygen  
concentration in this film.

1. A method of forming titanium silicide films in-situ  
over a substrate in a  
cold walled reactor comprising the step of:

(e) promptly thereafter selectively heating the substrate  
and polysilicon layer  
by radiant thermal energy from an incoherent infra-red  
heater to bring the  
substrate and layer to a predetermined temperature above  
500.degree. C.  
suitable for formation of a titanium silicide layer on said  
polysilicon layer  
while maintaining the reactor walls at a substantially  
lower temperature;

(f) introducing a gaseous silicon atom containing reactant  
and a gaseous  
titanium atom containing reactant into the reactor at a  
suitable pressure to  
form a layer of titanium silicide on said layer; said  
titanium silicide layer,  
as deposited, being smooth and having a minimum resistivity  
of 22 microohms-cm  
to a value of approximately 39 microohms-cm.

Article entitled, "Plasma-Enhanced CVD of Titanium  
Silicide", J. Vac. Sci.  
Technol., B 2 (4), Oct.-Dec. 1984, pp. 733-737.

L Number	Hits	Search Text	DB	Time stamp
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9	115	((plasma with (nitrogen or hydrogen or ammonia)) same cleaning) and substrate and silicide	USPAT; US-PGPUB	2003/03/06 16:03
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11	28	((plasma with (nitrogen or hydrogen or ammonia)) same cleaning) and substrate and silicide) and @ad<=19980407) and selective\$2	USPAT; US-PGPUB	2003/03/06 16:07

US-PAT-NO: 6001736

DOCUMENT-IDENTIFIER: US 6001736 A

TITLE: Method of manufacturing semiconductor device and an apparatus for manufacturing the same

----- KWIC -----

The CVD method may be classified into a selective deposition type CVD method and a blanket deposition type CVD method. In the selective deposition type CVD method, there are formed on a substrate surface a non-conductive area (e.g. a surface of an insulating layer formed on a lower wiring metal layer) and a conductive area (e.g. a surface of a lower wiring layer exposed in a bottom of a contact hole) and a wiring metal is deposited selectively on the conductive area. In the blanket deposition type CVD method, an underlying metal film such as a titanium nitride film is first formed on a whole surface of the substrate and then a wiring metal is deposited on the titanium nitride film by the CVD method. In the blanket deposition type CVD method, a sensitivity to a surface condition is low, so that the wiring metal film can be manufactured stably in a mass production. Furthermore, in the blanket deposition type CVD method, a metal wiring layer may be simply formed by patterning wiring metal film and the underlying metal film deposited on the flat surface of the insulating layer surrounding the contact hole.

The method of depositing tungsten within a contact hole by the selective deposition type CVD method has been described in the

following publication.

(4) Use is made of a deposition apparatus including a cleaning chamber and a CVD chamber connected with each other by means of an air-tight passageway. At first, a substrate is placed in the cleaning chamber and a metal surface exposed at a bottom of a contact hole is cleaned by means of plasma containing hydrogen or halogen gas. Then the substrate is transferred into the CVD chamber via the air-tight passageway without being exposed to the atmosphere, and after that tungsten is deposited selectively within the contact hole by the CVD method using tungsten hexafluoride as a source material. This known method has been proposed in U.S. Pat. No. 5,043,299 to Chang et al.

In case of forming a wiring metal layer, a wiring metal film such as an aluminum alloy film is formed on a whole surface of an underlying insulating layer, and then the metal film is changed into a desired pattern by removing selectively a part of the metal film by means of photolithography and dry etching. However, recently a width of a wiring pattern has become thinner and thinner, so that it has become difficult to perform the dry etching for the wiring metal film. In order to solve such a problem, in U.S. Pat. No. 4,789,648 there has been proposed another known method, in which a thin recess or groove is formed in a surface of an insulating layer and a wiring member is selectively formed within the groove. Also in this case, the CVD method could be advantageously utilized for filling the thin groove with a wiring metal.

According to the invention, by effecting the sputter etch effect of the hydrogen plasma, not only the contaminants adsorbed on the

surface of the underlying metal film are removed, but also a surface area of the underlying metal films is increased by forming atomic level depressions and protrusions and by etching weak portions such as grain boundaries or the surface of the underlying metal film. Therefore, the hydrogenation is enhanced. The sputter etching is particularly effective when the underlying metal film is made of more than two elements. A refractory metal compound such as titanium nitride has a substantially stoichiometric atomic ratio in a bulk, and this is retained also in a surface area. In this case, valence electrons of atoms constituting the compound just fill the Brillouin zone, so that no excess and vacancy are existent. When the surface is sputter-etched by the bombardment of hydrogen ions, among the atoms constituting the compound an atom which is liable to be etched is selectively or predominantly etched. Which of the atoms is predominantly etched is dependent upon process conditions and a kind of compound, but in general a light atom is predominantly etched.

The inventors of the present application have conducted various experiments and analyses upon the hydrogen plasma treatment and the successive MO-CVD (Metal Organic CVD) process, and have found that a deposition of a wiring metal during the MO-CVD process is strongly influenced by conditions of the plasma treatment. When the underlying metal film is made of titanium nitride, a deposition speed of a wiring metal on a flat surface portion is kept relatively high under a low plasma power density. In this case, by utilizing the cleaning effect of the hydrogen plasma upon inner walls of an opening, a surface condition of the underlying metal film on the flat surface

portion can be made identical with that on the inner walls of the opening. Therefore, a deposition of a wiring metal film on the flat surface portion and a formation of a plug within the opening can be performed simultaneously.

In the known method described in the above mentioned publication of Chang et al teaching the hydrogen plasma treatment for improving the selective CVD of tungsten, a deposition is enhanced buy cleaning the surface of the titanium nitride film. According to the invention, the hydrogen plasma treatment is carried out for introducing the delay time in a deposition of aluminum on the flat surface portion, so that a time at which the mouth of the contact hole is clogged by the deposited aluminum is prolonged and during this delay time period the contact hole can be sufficiently filled with aluminum. According to the invention, it is experimentally confirmed that this merit can be attained only by the hydrogen plasma treatment under a given condition.

the surface of the underlying metal film includes a refractory metal compound selected from the group consisting of a nitride, an oxide, a carbide, a boride, and a silicide of the refractory metal; and

the surface of the underlying metal film includes a refractory metal compound selected from the group consisting of a nitride, an oxide, carbide, a boride, and a silicide of the refractory metal; and

T. Kosugi et al., "Novel Si Surface Cleaning Technology with Plasma Hydrogenation and Its Application to Selective CVD-W Clad Layer Formation", 1995 Symposium on VLSI Technology Digest of Technical Papers, NTT LSI Laboratories, 1995, pp. 41 and 42.

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US-PAT-NO: 6090709

DOCUMENT-IDENTIFIER: US 6090709 A

TITLE: Methods for chemical vapor deposition and preparation of conformal titanium-based films

----- KWIC -----

Chemical vapor deposition (CVD) is a process whereby a solid film is synthesized from the reaction products of gaseous phase precursors. The energy necessary to activate the precursors and thereby start the chemical reactions which lead to film formation, may be thermal and/or electrical, and may be reduced by catalytic activity at the surface of the substrate to be coated. It is this reactive process which distinguishes CVD from physical deposition processes, such as sputtering or evaporation. CVD potentially offers many intrinsically attractive features for fabrication of Ti and TiN films as demanded by modern microelectronics. For example, CVD can generally provide a high growth rate and conformal coating of substrates having a complex topography of trenches and vias. In addition, catalysis interaction of the substrate with CVD source precursors can possibly lead to selective metal growth.

As used herein, the term "titanium-based film" refers to a film containing titanium. Exemplary titanium-based films include films of titanium metal, titanium nitride, titanium silicide and laminates thereof including a bilayer film of titanium metal and titanium nitride. The

titanium-based films of the invention may be substantially pure, or may contain a mixture of phases of titanium-based materials, e.g., a mixture of titanium metal phases with titanium nitride or titanium silicide phases. In addition, the titanium-based films of the invention may contain gas molecules, for example, nitrogen.

The substrate 26 is placed into the CVD reactor and then preferably exposed to a cleaning regime. Pre-deposition substrate cleaning is preferably accomplished by exposing the substrate in situ to a hydrogen plasma having a plasma power density of about 0.1 to about 1.0 W/cm.<sup>sup.2</sup>. Substrate cleaning as described is performed for both TCVD and PPCVD.

The appearance and composition of the titanium-based films prepared according to the inventive methods, as well as their structural and electrical properties, will be described next. It should be noted that the formation of titanium silicide films (TiSi), occurs only when the substrate is silicon or polysilicon and the titanium being deposited is particularly pure titanium metal. In such cases, the substrate-titanium interface can react to form a layer of TiSi. It has been observed that a silicon substrate can catalyze the reaction(s) leading to the deposition of titanium metal.

Titanium and titanium silicide films were prepared in the deposition reactor shown in FIG. 1, according to the PPCVD method of the invention. The source precursor was titanium tetraiodide and it was sublimed at a temperature within the range of 120.degree. C. to 160.degree. C. Films were prepared during reactions wherein the working pressure inside the deposition reactor was from 200 to 400 mtorr, the carrier gas was hydrogen with a flow

rate of from 10 to 60 sccm, the auxiliary gas was argon with a flow rate of 400 to 600 sccm and the substrate temperature was from 300.degree. C. to 450.degree. C. The films were deposited onto a silicon wafer.

The titanium and titanium silicide films thus produced were metallic, continuous, and silver colored. X-ray diffraction (XRD) analysis of a Ti film grown at 450.degree. C. is shown in FIG. 6 for a 1000 .ANG.-thick film on Si. The XRD analysis shows that the film has a hexagonal Ti phase. X-ray photoelectron spectroscopy (XPS) was performed using a Perkin-Elmer Physical Electronics Model 10-360 spherical capacitor analyzer. The gold f.sub.7/2 line at 83.8 eV was taken as reference line and the analyzer calibrated accordingly. All spectra were obtained using a pass energy of 5 eV at a resolution of 0.8 eV. A primary x-ray beam (Mg K.alpha., 127 eV) of 15 keV and 300 W was employed. The analysis chamber pressure was in the 10.sup.-10 torr range, and the results were standardized using a sputtered Ti sample. The XPS survey spectra (FIG. 7) indicated that, within the detection limits of XPS, the Ti films produced below 400.degree. C. contained less than 20 atomic percent oxygen, while Ti films produced above 400.degree. C. were free of oxygen and exhibited significant interactions with the Si substrate, which requires pure Ti to occur. No carbon or any other light element contaminants were observed in the films, regardless of substrate temperature. As used herein, light elements refer to elements having atomic number between 3 and 13, inclusive. The presence of iodine was detected at levels of about 0.4 to 1.5 atomic percent. Four-point probe resistivity measurements found that film

resistivities as low as 90  $\mu\Omega\cdot\text{cm}$  could be obtained.

The nature of the titanium and titanium silicide films vis-a-vis a silicon substrate was next examined. The adherence of the titanium films to either silicon or silicon dioxide was observed to be good. Cross-section SEM analysis was carried out on a Zeiss DSM940 microscope, employing a 20 keV primary electron beam and a beam current of 4  $\mu\text{A}$ . An SEM micrograph (FIG. 8) of a 1000  $\text{\AA}$ -thick Ti film showed conformal step coverage of 0.20  $\mu\text{m}$  vias with aspect ratio of 6.

The substrate (wafer) 26 was placed on the lower, grounded plasma electrode 24, and was heated to 425 $^{\circ}\text{C}$ . by an 8" boron nitride (BN)-encapsulated graphite heater 27. A hydrogen plasma was used for in-situ pre-deposition substrate cleaning at a plasma power density of 0.25  $\text{W}/\text{cm}^2$ , while no plasma was employed during actual deposition. A specially designed shower head 28 and associated pumping lines 29 were employed to ensure proper reactant mixing and uniformity in reactant delivery and flow over the 8" wafer.

In this case, plasma-promoted CVD (PPCVD) was employed for the growth of Ti thin films. Accordingly, a hydrogen plasma was used for in situ pre-deposition substrate cleaning at a plasma power density of about 0.25  $\text{W}/\text{cm}^2$ , while an argon plasma was employed during actual deposition at a plasma power density of about 0.25  $\text{W}/\text{cm}^2$ . The side line 33 was employed to feed the argon (Ar) gas into the reactor. The argon flow of 500 liters/minute was controlled by the mass flow controller 34 and associated isolation valve 35. The substrate (wafer) 26 was placed on the lower, grounded plasma electrode 24, and was

heated to 450.degree. C. by an 8" boron nitride  
(BN)-encapsulated graphite  
heater 27.